

PATENT SPECIFICATION

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(54) MANUFACTURE OF HALOGENATED HYDROCARBONS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the manufacture of tetrafluoroethane.

According to the present invention we provide a process for the manufacture of tetrafluoroethane having the formula CHF_2CHF_2 or $\text{CF}_3\text{CH}_2\text{F}$ characterised in that a haloethane having four or five fluorine atoms of formula CF_2XCFYZ where X is fluorine or chlorine and when X is fluorine, Y is chlorine or fluorine and when Y is chlorine Z is chlorine, fluorine or hydrogen and when Y is fluorine Z is hydrogen and when X is chlorine Y is fluorine and Z is either chlorine or hydrogen is reacted with hydrogen at elevated temperature in the presence of a hydrogenation catalyst.

The organic starting materials of the present invention consist of:—

- 1,2-dichloro-1,1,2,2-tetrafluoroethane ($\text{CClF}_2\text{CClF}_2$)
- 1,1-dichloro-1,2,2,2-tetrafluoroethane ($\text{CCl}_2\text{F}_2\text{CF}_3$)
- 1-chloro-1,1,2,2,2-pentafluoroethane (CClF_2CF_3)
- 1-chloro-1,2,2,2-tetrafluoroethane ($\text{CHClF}_2\text{CF}_3$)
- 2-chloro-1,1,2,2-tetrafluoroethane ($\text{CHF}_2\text{CClF}_2$)
- 1,1,2,2,2-pentafluoroethane (CHF_2CF_3)

Mixtures of said organic starting materials may be employed. Two very suitable starting materials are 1,2-dichloro-1,1,2,2-tetrafluoroethane (the asym isomer of dichloro-tetrafluoroethane, $\text{CClF}_2\text{CClF}_2$) and 1,1-dichloro-1,2,2,2-tetrafluoroethane (the asym isomer of dichloro-tetrafluoroethane, $\text{CCl}_2\text{F}_2\text{CF}_3$). 1,2-dichloro - 1,1,2,2-tetrafluoroethane containing a small proportion (e.g. up to 10% by wt) of 1,1-dichloro - 1,2,2,2-tetrafluoroethane) as produced commercially may be used as organic starting materials. Alternatively mixtures of said dichloro-tetrafluoroethanes in any proportions may be employed. In the present process there is removal of two chlorine atoms or a chlorine and/or a fluorine atom from the haloethane starting material and substitution of hydrogen therefore. Hydrogenation catalysts are in themselves known. Examples of hydrogenation catalysts include nickel or metals of Group VIIIA of the Periodic Table or oxides or salts thereof.

In use a compound of such a metal is reduced at least in part to the metal. One very useful metal which can be employed in the process of the present invention is palladium. The metal may be carried on a suitable support, for example, alumina or activated carbon.

The proportion of hydrogen to organic feed is capable of considerable variation. Usually at least the stoichiometric amount of hydrogen is employed to remove the halogen atom or atoms. Considerably greater than said stoichiometric amounts for example 4 or more moles of hydrogen may be employed per mole of starting material. When the organic starting materials consists of essentially pure 1,2-dichloro - 1,1,2,2-tetrafluoroethane ($\text{CClF}_2\text{CClF}_2$) or 1,1-dichloro - 1,2,2,2-

5 tetrafluoroethane (CCl_2FCF_3) it is preferred to employ at least two moles of
hydrogen (the stoichiometric amount) per mole of organic starting material. When
a mixture of $\text{CClF}_2\text{CClF}_2$ and CCl_2FCF_3 is employed as organic feed there may be
employed at least the stoichiometric amount of hydrogen per mole of CCl_2FCF_3 .
10 This can mean that there is sometimes less than the stoichiometric amount of
hydrogen with respect to total mole fluorochloroethane feed. Thus with a mixture
containing 3 moles $\text{CClF}_2\text{CClF}_2$ and 1 mole CCl_2FCF_3 there may be employed 2 to
3 moles of hydrogen per mole CCl_2FCF_3 and this corresponds to a molar ratio of
hydrogen to total mole fluorochloroethane feed of 0.55:1 to 0.75:1 respectively.
15 Similarly when there is employed an equimolar mixture of $\text{CClF}_2\text{CClF}_2$ and
 CCl_2FCF_3 there may be employed 2 to 3 moles of hydrogen per mole CCl_2FCF_3
and this corresponds to a molar ratio of hydrogen to total mole fluorochloroethane
feed of 1:1 to 1.5:1. On the other hand with a mixture of 3 moles $\text{CF}_2\text{ClCF}_2\text{Cl}$ and 1
mole CCl_2FCF_3 there may be employed 3 moles H_2 per total mole of total
fluoroethane and this corresponds to 12 moles H_2 per mole CCl_2FCF_3 .

Atmospheric or superatmospheric pressures may be employed.

The reaction is suitably carried out in the vapour phase at a temperature which
is at least 200°C and not greater than 450°C . Preferably the reaction temperature is
in the range 225°C to 400°C .

Contact times are usually in the range 5 to 60 seconds especially 5 to 30
seconds when the reaction is carried out in the vapour phase.

The tetrafluoroethane product obtained depends to a considerable extent on
the choice of starting material. When the organic starting material is 2,2-dichloro-
1,1,1,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane (asym tetrafluoroethane;
25 $\text{CF}_3\text{CH}_2\text{F}$) is obtained almost to the exclusion of 1,1,2,2-tetrafluoroethane (sym
tetrafluoroethane, CHF_2CHF_2). When the organic starting material is 1,2-
dichloro-1,1,2,2-tetrafluoroethane the reaction product usually comprises a
mixture of the two isomers of tetrafluoroethane. As the proportion of 2,2-dichloro-
1,1,1,2-tetrafluoroethane with respect to 1,2-dichloro-1,1,2,2-tetrafluoroethane is
increased in a mixture thereof increased amounts of the asymmetrical isomer
30 $\text{CF}_3\text{CH}_2\text{F}$ is formed. Also an alumina support is especially useful for the
manufacture of $\text{CF}_3\text{CH}_2\text{F}$ while an activated carbon support is especially useful in
the manufacture of a mixture of $\text{CF}_3\text{CH}_2\text{F}$ and CHF_2CHF_2 .

In the present process hydrogen and organic by-products, for example, 2-
chloro-1,1,1,2-tetrafluoroethane may be recycled to the process. The desired
products of the present invention may be separated by conventional means e.g. by
fractional distillation. Unreacted 1,2-dichloro-1,1,2,2-tetrafluoroethane may if
desired be tapped off and used as a refrigerant.

The present process has the advantages that the desirable 1,1,1,2-
tetrafluoroethane, 1,1,2,2-tetrafluoroethane or mixtures thereof in various
proportions can be obtained by a simple and convenient method. Desired products
can be obtained in high degree of purity with good conversions of the fluoro-
chloroethane starting material.

The following Examples illustrate the invention:—

Example 1.

45 Into a heat-resistant glass tube 30 cms long and 2.5 cms internal diameter,
surrounded by an electric furnace, were centrally placed 40 mls of a particulate
catalyst consisting of palladium supported on charcoal. This catalyst was intimately
mixed with 40 mls glass helices to prevent clogging of the catalyst. The palladium
50 was present in the proportion 5% by weight with reference to the charcoal.

Hydrogen and dichlorotetrafluoroethane (96.5% by weight, 1,2-dichloro -
1,1,2,2-tetrafluoroethane; 3.5% by weight, 1,1-dichloro - 1,2,2,2-tetrafluoro-
ethane) at a molar ratio of 2:1 were passed through the heated tube, the catalyst
bed being maintained at various reaction temperatures. The flow rates of organic
material and hydrogen were 50 cc/min and 100 cc/min, respectively. The % v/v of
55 organic materials in the exit gas was determined by gas liquid chromatography.

The other reaction conditions and composition of the organic products were
as shown in Table 1.

TABLE I

Product % v/v	Temperature °C			
	240	300	330	370
	Contact time (secs.)			
	17.9	16.3	15.6	14.6
CF ₃ CH ₂ F	6.1	9.2	9.8	11.4
CHF ₂ CHF ₂		4.4	8.9	11.7
CHF ₂ CClF ₂ / CHClFCF ₃	3.6	20.1	21.3	21.4
CClF ₂ CClF ₂ / CCl ₂ FCF ₃	89.2	64.8	57.3	46.2
CF ₃ CH ₃	0.6	1.5	2.2	3.3
Others			0.5	5.9

Example 2.

The procedure of Example 1 was essentially repeated but with a molar ratio of H₂:organic starting material of 3:1. The flow rates of organic material and hydrogen were 50 cc/min and 150 cc/min, respectively. The other reaction conditions and composition of the organic products were as shown in Table II.

TABLE II

Product %v/v	Temperature °C			
	240	255	300	325
	Contact time (secs.)			
	12.8	12.4	11.4	11.0
CF ₃ CH ₂ F	11.3	9.9	9.7	8.1
CHF ₂ CHF ₂	7.4	17.6	29.6	35.9
CHF ₂ CClF ₂ / CHClFCF ₃	40.5	48.9	40.1	39.5
CClF ₂ CClF ₂ / CCl ₂ FCF ₃	39.4	21.4	17.3	10.8
CF ₃ CH ₃	1.4	1.8	2.1	3.1
Others		0.3	1.2	2.6

} fully hydrogenated
material
mono-hydrogenated
material
starting material

Example 3.

The general procedure of Example 2 was repeated but with 1,1-dichloro-1,2,2,2-tetrafluoroethane as organic starting material. The other reaction conditions and composition of the organic products were as indicated in Table III.

TABLE III

Product %v/v	Temperature °C	
	285	310
	Contact time (secs.)	
	12.5	12.0
CF ₃ .CH ₂ F	71.7	72.0
CHF ₂ .CHF ₂	0.9	0.3
CHClFCF ₃ /CF ₂ ClCF ₂ H	8.1	6.1
CCl ₂ FCF ₃ /CClF ₂ .CClF ₂	11.0	5.7
CF ₃ .CH ₃	8.3	15.9

Example 4.

The general procedure of Example 2 was repeated but with a mixture of 1,2-dichloro-1,1,2,2-tetrafluoroethane, (72% by weight) and 1,1-dichloro-1,2,2,2-tetrafluoroethane (28% by weight) as organic starting material. The molar ratio of H₂: the mixed organic starting material was 3:1. The flow rates of hydrogen and organic starting material were 150 cc/min and 50 cc/min, respectively. The reaction temperature was 300°C. The contact time was 12 seconds.

The composition of the organic product was as given in Table IV.

TABLE IV

Product % v./v	
CF ₃ .CH ₂ F	37.6
CHF ₂ CHF ₂	14.9
CHF ₂ CClF ₂ /CHClFCF ₃	26.8
CF ₃ .CH ₃	13.0
CClF ₂ CClF ₂ /CFCI ₂ CF ₃	7.7

Example 5.

The general procedure of Example 4 was repeated except that the flow rate of hydrogen and the mixed organic starting material and hydrogen was 100 cc/min and 33 cc/min, respectively, and the contact time was 18 seconds.

The composition of the organic product was as given in Table V.

TABLE V

Product % v./v	
CF ₃ CH ₂ F	46.2
CHF ₂ CHF ₂	8.0
CHF ₂ CClF ₂ /CHClFCF ₃	26
CF ₃ CH ₃	8.2
CClF ₂ CClF ₂ /CFCI ₂ CF ₃	11.3

Example 6.

The general procedure of Example 5 was repeated except that the flow rates of hydrogen and organic starting material were 90 cc/min and 30 cc/min, respectively, the contact time was 19 seconds and the reaction temperature was 350°C.

The composition of the organic product was as given in Table VI.

TABLE VI

Product % v/v	
CF ₃ CH ₂ F	41.8
CHF ₂ CHF ₂	16.3
CHF ₂ CClF ₂ /CHClFCF ₃	24.8
CF ₃ CH ₃	11.8
CClF ₂ CClF ₂ /CFCI ₂ CF ₃	5.3

Example 7.

The general procedure of Example 2 was repeated but with 2-chloro-1,1,1,2-tetrafluoroethane as starting material. The other reaction conditions and composition of the organic product were as indicated in Table VII.

TABLE VII

Product % v/v	Temperature °C		
	280	350	420
	Contact time (secs.)		
	13	11	10
CF ₃ CH ₂ F	82.0	94.1	95.8
CHF ₂ CHF ₂	0.8	0.8	0
CF ₃ CH ₃	1.4	2.9	3.3
CHClFCF ₃	15.7	2.3	0
C ₂ F ₄	0	9	0.9

CF₂-CHFCl

product of hydrodechlorination

starting material

Example 8.

The apparatus comprised a heat-resistant glass tube 30 cms long and 2.5 cms internal diameter surrounded by an electric furnace. Two particulate catalysts were employed which consisted of palladium (2% w/w and 5% w/w) supported on alumina.

Hydrogen and a mixture of 1,2-dichloro-1,1,2,2-tetrafluoroethane (72% by weight) and 1,1-dichloro-1,2,2,2-tetrafluoroethane (28% by weight) were passed over the catalyst under various reaction conditions as disclosed in Table VIII. The molar ratios of hydrogen with respect to total dichlorotetrafluoroethane starting material for Runs 1, 2 and 3 were 0.5:1, 0.5:1 of 0.75:1, respectively. The flow rates of H₂ and CCl₂FCF₃ for these Runs were 50 and 25 cc/min, 50 and 25 cc/min, and 63 cc/min and 21 cc/min, respectively. The % v/v of organic materials in the exit gas was determined by gas liquid chromatography.

TABLE VIII

Product % v/v	Run 1	Run 2	Run 3
	Temperature °C		
	300	295	300
	Contact time (secs)		
	10.6	10.3	16.3
	% Pd in catalyst (w/w)		
	2	5	2
	Molar Ratio H ₂ : CFCI ₂ CF ₃		
	2:1	2:1	3:1
CF ₃ CH ₂ F	20	18.8	24.9
CHF ₂ CHF ₂	—	—	—
CHClFCF ₃ /CHF ₂ CClF ₂	2.6	0.4	0.3
CF ₃ CH ₃	0.4	0.5	0.3
CClF ₂ CClF ₂ /CFCI ₂ CF ₃	62.5	71.9	64.4
Other fluorochlor water C ₂ compounds	10.9	5.7	8.0

Example 9.

The apparatus comprised a vertical 'Inconel' tube ('Inconel' is a Registered Trade Mark) of 7.5 cms internal diameter. The tube was packed to a height of 90 cm with a catalyst in the form of sphere (3 mm diameter) consisting of 2% w/w Pd supported on alumina.

Hydrogen and a mixture of 1,2-dichloro-1,1,2,2-tetrafluoroethane (50% by weight) and 1,1-dichloro-1,2,2,2-tetrafluoroethane (50% by weight) were passed upwardly through the static catalyst under various process conditions as disclosed in Table IX. The molar ratios of hydrogen with respect to total dichloro-tetrafluoroethane starting material for Runs 1, 2 and 3 were 1.45:1, 1.6:1 and 1.6:1, respectively. The flow rates of H₂: CFCI₂CF₃ for these runs were 3.14 l and 0.98 l/min, 3.81 l and 1.15 l/min and 3.8 l and 1.15 l/min, respectively.

TABLE IX

Product v/v	Run 1	Run 2	Run 2
	Temperature °C		
	250	275	330
	Contact time (secs)		
	30	20	20
	Molar ratio H ₂ : CFCI ₂ CF ₃		
	3.2:1	3.2:1	3.3:1
CF ₃ CH ₂ F	46.1	35.5	26.8
CHF ₂ CHF ₂	—	—	—
CHClFCF ₃ /CHF ₂ CClF ₂	3.4	5.4	2.0
CF ₃ CH ₃	1.6	1.9	1.2
CClF ₂ CClF ₂ /CFCI ₂ CF ₃	45.8	54.6	69
Other fluorochloro C ₂ compounds	0.5	0.5	0.4

1,1,1,2-tetrafluoroethane was recovered from the crude reaction product by distillation in a glass apparatus consisting of a boiler, surmounted by a fractionation column having 40 theoretical plates, a reflux divider and condenser. The apparatus was operated at atmospheric pressure and after removal of lights boiling at -40°C to -27°C said 1,1,1,2-tetrafluoroethane was recovered as a top-product boiling at -26°C.

Example 10.

The apparatus comprised a mild steel tube (5 cms diameter) packed through 300 cms of its length with a catalyst in the form of spheres (3 mm diameter) consisting of 2% w/w Pd supported on alumina.

5 Kgs per hour of a mixture of 1,2-dichloro-1,1,2,2-tetrafluoroethane (50% by weight) and 1,1-dichloro-1,2,2,2-tetrafluoroethane (50% by weight) and 770 l/hour of hydrogen were passed upwardly through the static catalyst. The pressure was 5 Bars gauge. The temperature of the catalyst bed was maintained by a molten salt bath at 340°C. The contact time was 51 seconds. The molar ratio of hydrogen with respect to total dichlorotetrafluoroethane starting material was 1.1:1, the molar ratio of hydrogen with respect to 1,1-dichloro-1,2,2,2-tetrafluoroethane being 2.2:1.

The organic reaction produced after washing with dilute caustic soda solution and drying over calcium chloride was condensed at -70°C and comprised (v/v):

25%	CF ₃ CH ₂ F
5%	CF ₃ CH ₃
5%	CHClFCF ₃
65%	CF ₂ ClCF ₂ Cl/CF ₃ CFCl ₂

WHAT WE CLAIM IS:—

1. A process for the manufacture of tetrafluoroethane having the formula CF₃CH₂F or CHF₂CHF₂ characterised in that a haloethane having four or five fluorine atoms of formula CF₂XCFYZ where X is fluorine or chlorine and when X is fluorine, Y is chlorine or fluorine and when Y is chlorine Z is chlorine, fluorine or hydrogen and when Y is fluorine Z is hydrogen and when X is chlorine Y is fluorine

and Z is either chlorine or hydrogen is reacted with hydrogen at elevated temperature in the presence of a hydrogenation catalyst.

2. A process as claimed in Claim 1 characterised in that the haloethane starting material is 1,2-dichloro-1,1,2,2-tetrafluoroethane.

3. A process as claimed in Claim 1 characterised in that the haloethane starting material is 1,1-dichloro-1,2,2,2-tetrafluoroethane.

4. A process as claimed in Claim 1 characterised in that the haloethane starting material is a mixture of 1,2-dichloro-1,1,2,2-tetrafluoroethane and 1,1-dichloro-1,2,2,2-tetrafluoroethane.

5. A process as claimed in Claim 4 characterised in that the molar ratio of 1,2-dichloro-1,1,2,2-tetrafluoroethane to 1,1-dichloro-1,2,2,2-tetrafluoroethane is in the range 3:1 to 1:1.

6. A process as claimed in any one of the preceding Claims 1 to 5 characterised in that at least the stoichiometric amount of hydrogen is employed to remove the halogen atom or atoms.

7. A process as claimed in any one of the preceding Claims 1 to 6 characterised in that there is employed up to four moles of hydrogen per mole of haloethane.

8. A process as claimed in Claim 5 characterised in that the molar ratio of 1,2-dichloro-1,1,2,2-tetrafluoroethane to 1,1-dichloro-1,2,2,2-tetrafluoroethane is 3:1 and in which there is employed 2 to 3 moles of hydrogen per mole of 1,1-dichloro-1,2,2,2-tetrafluoroethane corresponding to 0.5 to 0.75 moles hydrogen per total mole fluorochloroethane, respectively.

9. A process as claimed in Claim 5 characterised in that the molar ratio of 1,2-dichloro-1,1,2,2-tetrafluoroethane to 1,1-dichloro-1,2,2,2-tetrafluoroethane is essentially 1:1 and in which there is employed 2 to 3 moles of hydrogen per mole of 1,1-dichloro-1,2,2,2-tetrafluoroethane corresponding to 1 to 1.5 moles hydrogen per total mole fluorochloroethane, respectively.

10. A process as claimed in any one of the preceding claims characterised in that the hydrogenation catalyst is palladium.

11. A process as claimed in Claim 10 characterised in that the palladium is carried on an activated carbon support.

12. A process as claimed in Claim 10 characterised in that which the palladium is carried on an alumina support.

13. A process as claimed in any one of the preceding claims characterised in that the reaction is carried out in the vapour phase at a temperature of at least 200°C not greater than 450°C.

14. A process as claimed in Claim 13 characterised in that the reaction temperature is in the range 225°C to 400°C.

15. A process for the manufacture of 1,1,1,2-tetrafluoroethane and/or 1,1,2,2-tetrafluoroethane substantially as described with reference to the Examples.

16. 1,1,1,2-tetrafluoroethane and/or 1,1,2,2-tetrafluoroethane whenever manufactured by a process according to any one of the preceding claims.

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